

CHEMICAL REDUCTION OF SULFUR TRIOXIDE AND PARTICULATES FROM HEAVY OILS

Robert P. Bennett

Apollo Chemical Corporation, Whippany, New Jersey 07981

INTRODUCTION

There has been a significant increase in interest in the scientific application of fuel additives to residual fuel oils to solve fireside boiler problems, as well as additives to reduce air pollution from burning of residual fuels. This interest stems from: 1) restrictions on particulate and NO_x emissions imposed by the Environmental Protection Agency, 2) the higher price of fuel and the desire for increased efficiency, 3) the need to eliminate costly cold end corrosion, 4) community relations that require the eliminating of acid smut emissions and characteristic blue white plume caused by the condensation of SO_3 .

These fireside problems can be reduced or eliminated by instituting improved operating procedures plus the use of one or more additives added to the fuel oil or to the furnace burning the residual fuel.

Effective fuel additives have been shown to be limited to those that contain a metal. However, the choice of additive for any particular boiler depends upon the needs of the boiler and the particular environmental requirements.

In general, fuel additives should provide boiler cleanliness, high temperature vanadium corrosion protection, prevention of loss of operating capacity by maintaining design steam temperatures, cold end (air heater) corrosion protection, reduction of stack emissions from hydrocarbon particulate matter and SO_3 , and improvement in the handling characteristics of ash in the flue gas in oil-fired boilers equipped with precipitators and stack collectors. The significant fuel additives in use today usually contain MgO (with or without small amounts of aluminum oxide or hydrate), manganese, and MgO with manganese.

The use of magnesium oxide as a fuel additive, primarily for the control of vanadium slag, has been known for a number of years (1). The addition of MgO -based products to the fuel oil or furnace will raise the fusion point of the ash if used at a $\text{Mg}:\text{V}$ weight ratio of 1.5 to 1 (molar ratio of $\text{Mg}:\text{V}$ of 3:1). Properly treated ash will be soft, but voluminous. The increased ash burden on the boiler can lead to bridging and blockage in the boiler and increased particulate emissions. With today's low sulfur, low ash fuels, the use of MgO , at least as a slurry added to the fuel oil is no longer justified generally.

The purpose of this paper is to review the use of chemicals added to the fuel to improve combustion, thereby reducing unburned carbon particulate, and to reduce the formation of SO_3 in the flue gas, thereby reducing plume opacity and acid smut emissions.

Additionally, because additives in the fuel add to the ash burden of the boiler, an alternate approach for attacking the problems of cold end corrosion and acid smut emissions has been developed. This is a cold end feed of a properly constituted neutralizing additive, applied directly into the problem areas only and added strictly in proportion to the amount of SO_3 present in the flue gas, thus minimizing the treatment rate and reducing the problem of emissions to the atmosphere.

FUEL OIL TREATMENT

Sulfur in heavy fuel oil is oxidized readily to sulfur dioxide. A portion of this sulfur dioxide is further oxidized to sulfur trioxide. The extent of conversion of the SO_2 to SO_3 is dependent upon the percent of excess air and also on the presence of oxidation catalysts in the fuel, generally vanadium or nickel. Additionally, the boiler iron tube surfaces can themselves act as a catalyst for this reaction. The quantities of these catalysts will vary considerably in different fuel oils, so that the percent conversion, at any given level of excess air, will vary with the fuel and boiler cleanliness. It is difficult to predict the SO_3 content of the combustion products of a given fuel so, therefore, the exact dew point of the flue gas is difficult to forecast. An empirical correlation has been prepared as shown in Figure 1. It is similar to the experiences of others (2, 3, 6) who have shown the variation of SO_3 concentration as a function of O_2 concentration. Fuels examined have varied from a low vanadium content of below 50 parts per million up to fuels of 300 parts per million. Obviously, the best situation is to obtain the data for each particular unit. However, this graph has been extremely useful as a first approximation for a unit where test data are not available.

The sulfur content of the fuel oil obviously affects the parts per million of SO_3 in the flue gas. As expected, as the sulfur level of the fuel increases, so does the absolute amount of SO_3 in the flue gas up to a maximum level. Again, an empirical correlation of parts per million of SO_3 , in relation to the percent excess air and the sulfur in the fuel, can be obtained as shown in Figure 2. This also is similar to results of previous workers, such as Laxton (2), or Rendle et al. (7), both of whom used experimental furnaces. Note that a reduction in fuel sulfur from 2.5 to 1.5% results in a reduction in dew point of only about 7°F above an excess air of 10%.

From these two curves, it becomes obvious that in order to reduce SO_3 with any given fuel, the greatest effect would be obtained by reducing the percent excess air at which the unit is fired. Decreasing the excess air also has the advantage of decreasing BTU losses and increasing unit efficiency. However, excess air generally can only be reduced to a limited extent, before flue gas combustibles begin to increase rapidly. This in turn results in a decrease in efficiency or even unsafe firing conditions, as well as unsightly black plumes. The use of a combustion catalyst will reduce substantially the amount of combustibles in the flyash, and thus make it feasible to operate continuously at reduced or at low levels of excess oxygen. The latter in turn further reduces SO_3 generation.

An additional factor is that the use of a combustion catalyst, which is a metal, will also help to destroy the catalytic properties of the fuel metals by chemical reaction. Previous workers (1) have shown that operation at low excess air also favors the formation of the lower oxides of vanadium, V_2O_3 and V_2O_4 , which leads to high-melting ash and a minimum of corrosion and fouling.

The use of a manganese catalyst for the reduction of SO_3 is shown in Table 1. Note that at given oxygen levels (Units 2 and 3) there is a substantial reduction in SO_3 with treatment. The data for Unit 1 show both the reduction obtained from reduction of excess oxygen and the additional benefit of manganese treatment. The SO_3 content was determined by the well known EPA Method 8.

Particulate emissions consist of inorganic ash from the fuel, unburned carbon from incomplete combustion, and corrosion products. Flue gas ash loading from any particular fuel should be fairly constant at steady operating conditions. However, the carbon content can vary depending on the completeness of combustion and on excess air levels.

A number of metals are known to be effective as combustion catalysts. They can reduce particulate loadings if they promote more complete burning of the carbon portion. A recent paper by Giammar (4) points out the effectiveness of manganese for this purpose. It has been found that manganese can be used as an inorganic slurry (5,10) or in the form of a truly soluble organometallic species. The inorganic type is most economical for use in heavy fuels where higher concentrations of manganese are required, as compared to distillate fuels.

In a typical example, a refinery was required to burn heavy asphaltic bottoms in a package boiler producing 200,000 lbs. of steam per hour at 900°F superheat temperature and 900 psi. superheat pressure. Treatment of the pitch with 45 ppm Mn produced a decrease in flue gas particulates from 0.17 to 0.04 mg/SCF with a corresponding reduction of carbon content of the particulate from 72% to 31%.

For gas turbines and package boilers, the soluble form often becomes the additive of choice because of the ease in handling, particularly since the requisite parts per million of manganese is low enough so that the extra cost for supplying a soluble form of manganese is considered to be economical.

In addition to the reduction in acidic emissions and particulate emissions obtained by the use of a manganese combustion catalyst and reduced excess air level operations, there is often a significant increase in efficiency obtained. This can be directly translated into fuel savings and dollars as shown in Table 2. This efficiency increase alone often justifies the use of a fuel additive.

COLD END TREATMENT

So far, we have described the benefits of using fuel additives to reduce SO_3 emissions and to decrease unburned carbon particulate emissions. Even with these treatments, it has been found that a number of units suffer from varying degrees of cold end corrosion with resulting air heater blockage and wastage. Even with low sulfur fuels, many units experience cold end problems.

To minimize these problems one can reduce SO_3 content totally or raise the exit gas temperature above the dew point. Two methods of doing the latter are available: 1) steam coils in the air duct upstream of the air heater can be used to raise the temperature of the incoming air for combustion. This results in a higher metal temperature at the cold end of the air heater. 2) An air heater by-pass damper upstream of the air heater can be used to by-pass a portion of the incoming air for combustion around the air heater. This also results in a higher temperature at the cold end of the air heater. Both of these methods raise the exit gas temperature and sacrifice unit efficiency. A 40°F change in exit gas temperature is generally equivalent to 1% in unit efficiency.

An alternate, or supplementary treatment, depending on boiler operations, is the injection of a cold end, free-flowing, neutralizing powder (8), a process (10) which has been perfected over several years. This material is usually applied after the economizer and has the advantage of only being added in proportion to the free SO_3 present. In this way, the acidic conditions are neutralized with minimum burden on the system.

To illustrate the success of this approach, let us consider several case histories.

EXAMPLE I

A 220 MW pressurized unit with a Ljungstrom air heater had both severe corrosion and air heater pluggage problems which required a high exit gas temperature of 300°F to protect the cold end. The #6 fuel oil contained 400 ppm vanadium and 2.5% sulfur. Fuel use rate was 302 bbl/hour or 12,684 gallons per hour. MgO, in the form of a slurry, was added to the fuel oil in an attempt to solve the corrosion and pluggage problems and acid smut emissions. This approach was unsuccessful because of excess ash and blockage within the boiler. It was therefore decided to try cold end feed. The acid dew point of the untreated unit was 300°F, whereas the exit gas temperature was only 305°F. Using a feed rate of neutralizing agent of 0.19 lbs./bbl., the dew point was reduced to 180°F or essentially a water dew point. This allowed a safe reduction in exit gas temperature to 265°F by shutting off steam air preheaters and closing air heater by-pass ducts. The economic gain from these features alone was over \$200,000 annually. Additional benefits were reduced corrosion and maintenance costs and improved unit performance because of no air heater pluggage with treatment.

During the course of this investigation, we were again able to demonstrate that just the reduction in excess air alone is not sufficient to reduce the SO₃ to a low enough level to protect the cold end of the unit. Figure 3 shows the effect of excess air reduction on SO₃ generation in the untreated unit at constant load. Dropping the excess air level from 12 to 5% reduced the SO₃ content from 80 ppm to 30 ppm, but still resulted in a dew point of 290°F. Treatment with additive at 12% air reduced the SO₃ to 16 ppm and reduction to 5% air at the same treatment rate reduced the SO₃ to 2 ppm allowing safe operation at an exit gas temperature of only 265°F.

In considering a safe exit gas temperature, it must be remembered that it is not just the average cold end metal temperature, but the minimum metal temperature under the poorest operating temperatures and the duration of these conditions against which protection must be provided. By the use of the neutralizing additive, one not only stops the corrosion completely, but often also picks up the added economic benefits of being able to safely turn off water or steam air heaters and/or close air heater by-pass dampers.

EXAMPLE II

Even with low sulfur fuel (0.3%), units which cannot reduce excess air levels have a need for cold end protection. For example, a 350 MW pressurized boiler with a Ljungstrom air heater was experiencing significant cold end corrosion. This unit burned #6 oil of about 14 ppm vanadium and 0.3% sulfur. Excess air was 15%. Fuel consumption was 600 bbls./hr. or 25,200 gallons per hour. The exit gas temperature was 270°F, but the acid dew point was 273°F, equivalent to 10 ppm_v of SO₃. By applying the powdered neutralizing agent to the cold end ahead of the air heaters at a rate of 0.033 lbs./bbl, the dew point was reduced to 150°F or 0 ppm_v SO₃. By shutting the by-pass dampers, a 30°F reduction in exit gas temperature could be safely achieved. Fuel consumption alone has been cut by 14,000 bbls. a year, which at current prices is a savings of \$182,000.

CONCLUSIONS

In summary, we have reviewed the production of SO_3 and unburned particulate from burning heavy oils. Formation of SO_3 leads to corrosion of the cooler parts of the boiler, such as the air heater and duct work, and can produce a visible plume and acidic emissions. Unburned particulate leads to excessive emissions and a visible plume. Mechanical corrections alone usually are not sufficient to eliminate these problems. The use of a manganese combustion catalyst allows operation at low excess air levels, and consequently low SO_3 levels, without the adverse formation of unburned carbon particulate matter. The use of lower excess air levels improves unit efficiency and saves fuel.

Additionally, neutralization of residual SO_3 by application of a neutralizing additive in powder form into the cold end of the boiler allows operation at lower flue gas temperatures because of the lowered acid dew point. Air heaters and cold end duct work are thus protected while lower exit gas temperatures improve unit efficiency.

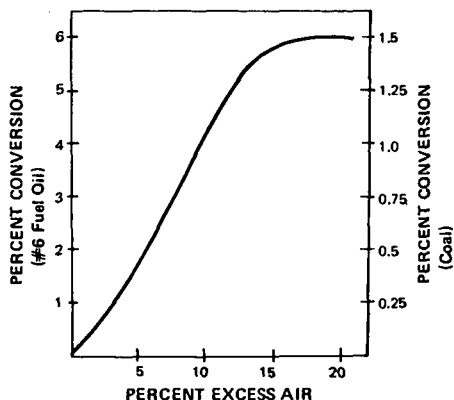
The combination of these two approaches: the use of chemical in the hot end for combustion improvement, and chemical in the cold end for acid neutralization, leads to significant savings with heavy fuel oil units while at the same time minimizing or eliminating emissions problems (9).

REFERENCES

1. Reid, W. T., "External Corrosion and Deposits," American Elsevier, New York, New York, 1971.
2. Laxton, J. W., in "The Mechanism of Corrosion by Fuel Impurities," Butterworths, London, 1963, pp. 228-237.
3. Reese, J. T., Jonakin, J., and Caracristi, V. Z., Combustion, **36**, 29, (1964).
4. Giammar, R. D., Krause, H. H., Locklin, D. W., ASME, 75-WA/CD-7.
5. Kukin, I., "Effects of Additives on Boiler Cleanliness and Particulate Emissions," International Meeting of the Society of Engineering Science, Tel Aviv, Israel, June 1972.
6. Kukin, I., and Bennett, R. P., "Chemical Reduction of SO_3 , Particulates and NO_x Emissions," The International Energy Engineering Congress, Chicago, Illinois, November 1975.
7. Rendle, L. K., Wilsdon, R. D., and Whittingham, G., Combustion, **31**, 30, (1959)
8. Kukin, I., and Ross, A., Combustion, **45**, 14, (1974).
9. U.S. Patent 3,837,820.
10. U.S. Patent 3,692,503.

FIGURE 1

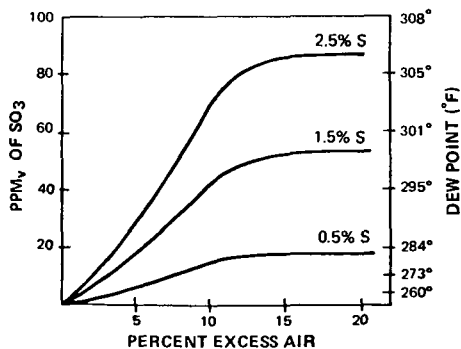
CONVERSION OF SULFUR TO SULFUR TRIOXIDE



EMPIRICAL PERCENT CONVERSION OF S TO SO_3 WITH VARYING EXCESS AIR FOR #6 OIL AND FOR COAL.

FIGURE 2

DEW POINT RELATED TO FUEL SULFUR CONTENT



SO_3 CONCENTRATION AND DEW POINT RELATED TO EXCESS AIR AND PERCENT FUEL SULFUR FOR #6 OIL.

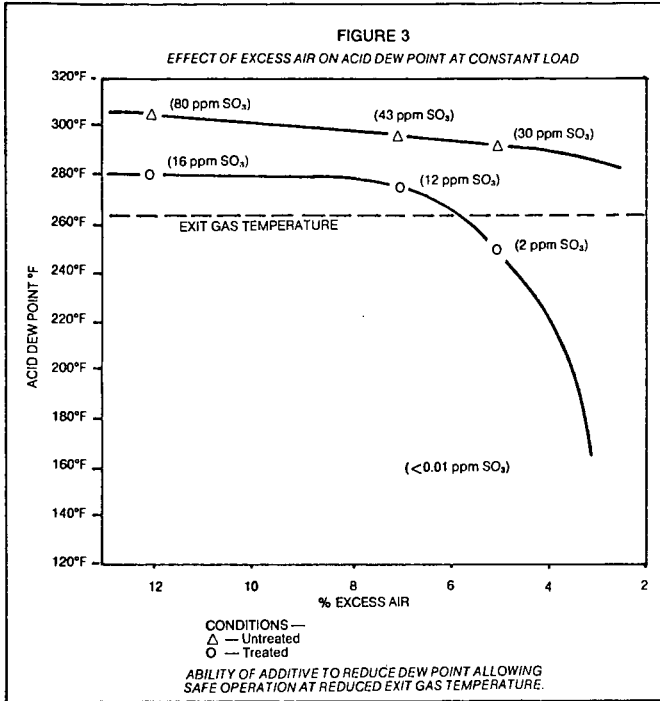


TABLE 1

EFFECT OF MANGANESE ON SO₃ GENERATION

Unit	% O ₂	SO ₃ (PPM at 3% O ₂)		Percent Reduction
		Untreated	Treated	
1	1.2	9.1	5.0	45.1
	1.7	14.2	8.0	43.7
	2.2	20.4	9.0	55.9
2	4.5 [±]	2.5	1.7	32.0
3	7.4	15.0	9.0	40.0

ABILITY OF MANGANESE TO REDUCE SO₃ CONCENTRATION IN
DIFFERENT UNITS AT VARIOUS EXCESS AIR LEVELS.

TABLE 2

FUEL SAVINGS FROM REDUCTION OF EXCESS
AIR ALLOWED BY USE OF MANGANESE ADDITIVES

Unit:	100 MW
Fuel:	#6 fuel oil with a heat value of 18,500 BTU/lb.
Fuel Use Rate:	Average 52,500 gallons/day
Excess Air:	30% Initial: 18.50 lbs. air/lb. of fuel 8% Final: 15.73 lbs. air/lb. of fuel/diff. = 2.77 lbs air
Additive:	31% Mn slurry at rate of 1 gallon/12,000 gallons fuel
Heat Capacity:	0.237 BTU/lb. of air/°F
Average Heat Loss:	Air to preheater = 85°F (ambient) Exit gas temp. = 275°F (average) ΔT = 190°F
BTU Savings:	{2.77 lbs. air/lb. fuel} {0.237 BTU/lb. air/°F} {190°F} = 124.7 BTU/lb. fuel oil Oil consumed (avg.) = 52,500 gal./day @ 8 lbs./gal. = 420,000 lbs./day @ 124.7 BTU/lb. = 52,374,000 BTU/day (saved)
Fuel Saved:	52,374 x 10 ⁶ BTU/day = 353.88 gal/day (saved) 148,000 BTU/gal. = 8.42 bbl./day At current price of \$11/bbl., this is worth \$92.62/day.